

P : not more than 0.03%,

S : not more than 0.05%,

Cr : 0.9 to 2.0%,

V : 0.03 to 0.3%,

Al : 0.003 to 0.10%,

N : 0.001 to 0.02%, and

O : not more than 0.003%,

wherein the balance comprises Fe and impurities, and

the carbon equivalent Ceq. (%) defined by the following equation is 0.60 to 0.85.

$$\text{Ceq.} = \text{C} + \text{Mn} / 6 + (\text{Cr} + \text{Mo} + \text{V}) / 5 + (\text{Ni} + \text{Cu}) / 15$$
, the non-heat treated seamless steel tube having a bainite-based structure.

Critical to note in this claim is the term "non heat treated", the carbon content, the manganese content, the vanadium content and the chromium content.

Turning now to the rejection, the Examiner has withdrawn the previous grounds of rejection in favor of JP 2003-64449 (JP '449). In making this rejection, the Examiner first alleges that the composition of JP '449 overlaps that which is claimed. Secondly, the Examiner contends that the composition of JP '449 would meet the claimed formula and therefore, the formula lends no patentable weight to the claim. Lastly, the Examiner recognizes that JP '449 teaches a heat treated steel, but contends that claiming a "non-heat treated steel" does not make a patentable distinction. As grounds for drawing this conclusion, the Examiner treats the claim as a product claim that is indistinguishable from the prior art product and Applicant has not yet established that

the claimed non-heat treated steel product is distinct from the prior art heat treated steel product.

Applicants assert that the heat treated steel of JP '449 does not render the non-heat treated steel of claim 1 obvious. The reason for the traversal is three-fold. First, basic metallurgical principles establish that a heat treated steel is not the same as a non-heat treated one. Evidence supporting this contention with accompanying arguments is submitted in this regard.

Secondly, there is no motivation to arrive at the invention given the teachings of JP '449 and this reference cannot establish a *prima facie* case of obviousness against claim 1.

Lastly, the Examiner cannot ignore the claim limitation of "non-heat treated" when considering the patentability of claim 1. When taking this limitation into account, JP '449 does not obviate claim 1.

On the first point, JP '449 discloses a heat resisting low alloy steel tube comprising a composition that could be considered similar to that claimed. Further, the steel tube is described as having a bainite structure. However, this is where the similarity ends since the steel tube of JP '449 is continuously heat treated. The Examiner admits to this point. In spite of this admission, the Examiner continues to assert that the steel of JP '449 would be the same but for a slight variation in composition, and that one of skill in the art would find it obvious to slightly alter the ranges of JP '449 so as to arrive at the claimed steel tube.

The flaw in this reasoning is characterizing the issue as one of a difference in composition only. The real issue is not only composition but structure, and whether the product of JP '449, taking into account composition and structure renders claim 1 obvious. The structural difference must be taken into account when examining claim 1, and when doing so, JP '449 does not teach that which is claimed.

In effect, the Examiner has given no weight from a claim structural standpoint to the fact that claim 1 is directed to a non-heat treated steel tube. Applicant contends that this is error when considering that which is well known in the art. That is, heat treating a steel is commonly recognized in metallurgy as a microstructure-changing event. Since this is fundamental aspect of metallurgy, claiming a "non-heat treated seamless steel tube" on its face does not require a further showing that the steel tube of claim 1 is different than the heat treated steel tube of JP '449.

Put another way, one of skill in the metallurgical arts would readily know that the structure of a non-heat treated tube of a given composition would not be the same as steel tube of the same composition that is heat treated. Even when the compositions are the same, which is not the case here, the steel microstructure would be different. This common knowledge directly contrasts with the Examiner's contention that, on its face, the heat treated steel of JP '449 and the non-heat treated steel of claim 1 are the same or similar. As between the two, the common knowledge in the art is the measuring rod, and when this rod is used, the only conclusion to be drawn is that the Examiner's contention that the only difference between JP '449 and claim 1 is a small

variation in composition is in error. This error fatally taints the rejection and requires its withdrawal.

In essence, the Examiner has placed the burden of showing that the claimed steel tube has a structure different from the prior art steel tube when common knowledge in the metallurgical arts already establishes this difference.

While it has been argued that common knowledge in the metallurgical arts says that it is improper to conclude that the heat treated steel tube of JP '449 is the same as claimed, Applicants provide evidence to support their position with respect to the common knowledge in the art. Submitted herewith is a copy of ISIJ International, Vol. 39 (1999), pp, 947-954. Particular reference should be made to Figures 7(a) and 7(b) and their relevant descriptions. These Figures show transmission electron micrographs of extraction replica from the specimens that are normalized or normalized and tempered, respectively. The specimen being examined is a steel having a composition of 0.06% C, 2.25% Cr, 1.6% W, 0.1% Mo, 0.25% V, and 0.05% Nb. It should be noted that this composition is similar to that at issue in this application.

The normalized specimen of Figure 7(a) shows Fe_3C type carbides inside the grains. In addition, fine precipitates of NbN and NbC have been identified.

In the normalized and tempered specimen of Figure 7(b), M_{23}C_6 type carbides are observed to precipitate along the former austenite grain boundaries. This carbide contains a higher amount of Fe.

Contrasting the normalized specimen with the normalized and tempered specimen, only fine Fe_3C type carbide is observed without M_{23}C_6 type carbides along the

former austenite grain boundaries in the normalized or non-heat treated steel. Moreover, the density of dislocations of the normalized but non-tempered steel is higher than that of the tempered steel tube. This comparison substantiates the contention that a heat treated steel tube does not have the same structure as a non-heat treated steel tube of the same composition. The submission of this evidence rebuts the Examiner's contention that the heat treated steel tube of JP '449 is the same or similar as the non-heat treated seamless steel tube claimed. Therefore, the Examiner must admit that JP '449 fails to teach a non-heat treated steel tube of the claimed composition, and thus also address this structural difference from an obviousness standpoint.

At this point, the Examiner could still contend that it would be obvious to omit the heat treating of JP '449. However, such an allegation lacks motivation to do so.

JP '449 explicitly teaches that the tube should be heat treated in a continuous heat treatment furnace to obtain the desired bainite structure so as to minimize the occurrence of flaws and improve high temperature strength. JP '449 teaches away from producing the steel in a non-heat treated form, and there can be no justification for omitting the heat treating step from JP '449. This teaching away further substantiates Applicant's contention that there is no legitimate basis to modify JP '449 to arrive at the invention.

In fact, the only source for such a modification would be the Applicant's invention and a rejection of this nature would be solely based on hindsight and thus improper.

The Examiner's attention in this regard is also directed back to the basics of the invention. What Applicant has done is to make a steel tube that has high strength and high toughness and prevents cracks from being generated at a welding part. This is accomplished by the following:

- 1) Control of the carbon so as to be less than 0.17%.
- 2) Refraining from heat treating of the steel.
- 3) Control of Mn in the range of 1.5-2.5%, control of Cr in the range of 0.9 to 2.0%, and control of V in the range of 0.03 to 0.3% in order to compensate the deterioration of strength because of the lowering of carbon content and providing a bainite based structure.

The invention as described above cannot be derived from JP '449 since there is no reason for the artisan to practice all of (1) to (3). As stated above, the only reason to arrive at the invention would be knowing the invention beforehand, and this cannot be the basis for a rejection under 35 U.S.C. § 103(a).

Lastly, the Examiner could allege that claim 1 is indistinguishable from JP '449 on the grounds that the preamble language of "A non-heat treated seamless steel tube" does not merit consideration from a patentability standpoint. Such an allegation would also be improper. MPEP Section 2110.02 explicitly states that any terminology in the preamble that limits the structure of the claimed invention must be treated as a claim limitation. This is clearly the case here and the Examiner cannot ignore the limitation in question when formulating a rejection under 35 U.S.C. § 103(a).

Admitting that JP '449 does not teach the claimed composition and having to examine the steel of claim 1 as a non-heat treated seamless steel tube, the cited reference cannot be relied upon under 35 U.S.C. § 103(a) to reject claim 1. Since claim 1 is patentable over the applied prior art, its dependent claims are also in condition for allowance.

Accordingly, the Examiner is respectfully requested to examine this application in light of this amendment, and pass claims 1-4 onto issuance.

If the Examiner believes that an interview with Applicant's attorney would be helpful in expediting prosecution of this application, the Examiner is invited to telephone the undersigned at 202-835-1753.

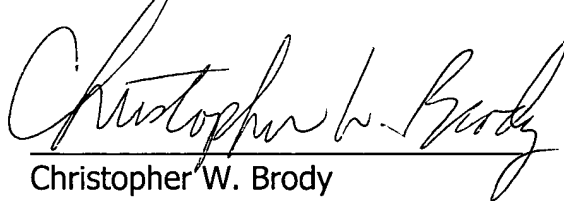
The above constitutes a complete response to all issues raised in the Office Action dated December 18, 2006.

Again, reconsideration and allowance of this application is respectfully requested.

Please charge any fee deficiency or credit any overpayment to Deposit Account No. 50-1088.

Respectfully submitted,

CLARK & BRODY

A handwritten signature in cursive script, reading "Christopher W. Brody", written over a horizontal line.

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Date: March 13, 2007

ISIJ International

Reprinted from Vol. 39 (1999), No. 9 (September)

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Effect of Trace Elements on Creep Properties of 0.06C–2.25Cr–1.6W–0.1Mo–0.25V–0.05Nb Steel

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(Received on April 20, 1999; accepted in final form on June 16, 1999)

The effect of trace elements such as Mn and B on creep properties of 0.06C–2.25Cr–1.6W–0.1Mo–0.25V–0.05Nb has been investigated from the standpoints of a long-term microstructural stability. The chemical analysis of extracted residues and TEM observation show that the $M_{23}C_6$ carbide and/or M_7C_3 carbides, precipitated by tempering are replaced by M_6C with a concentration of W; i.e., the amount of W in solution reduces during creep. On the other hand, MX type carbides such as VC and NbC are very stable during long-term aging and contribute to the creep strength by obstructing the dislocation annihilation.

One of the most significant results is that a reduction in Mn-content lowers the minimum creep rate, resulting in an increase in the creep rupture time. The nucleation and/or growth of M_6C are retarded with reducing Mn-content, thereby the increase in dissolved W seems to enhance the resistance to creep deformation. Another significant result is that an increase in B-content has delayed the transition from the primary creep to a tertiary creep stage. The principal roles of B are stabilizing $M_{23}C_6$ or $M_{23}(C,B)_6$ on former austenite grain boundaries and retarding the dynamic recrystallization during creep. In addition, in the specimens with higher amount of B, the bainite lath interface is covered by MX and some filmy precipitates with high density, thereby the softening resistance is enhanced.

KEY WORDS: heat resistant low alloy steel; creep; carbide; precipitation.

1. Introduction

A recent majority of the heat resistant steels used in the power plants is based on low-Cr steels containing Mo, W, V, and Nb so as to increase the creep resistance.¹⁾

Among low-Cr steels, a 0.06C–2.25Cr–1.6W–0.1Mo–0.25V–0.05Nb ferritic steel has extremely high creep strength as approximately 1.8 times of that of conventional 2.25Cr–1Mo steel by substituting W for a part of Mo and micro alloying V and Nb.^{2–4)} A reduction in C-content leads to a bainitic structure without martensitic phases, thereby allows it to be used in as-welded conditions without pre-weld and post-weld heat treatments. Field evaluation tests using utility boilers with a large capacity have shown that this steel is widely applicable for boiler materials, replacing conventional Cr–Mo steels.⁵⁾

The approaches to an increase in creep strength of the present steels are characterized as follows. (1) The stabilization of matrix must lead to the higher creep strength. (2) It has already been recognized that V and Nb precipitate as fine MX carbonitrides, which obstructed the motion of dislocations.^{6–7)} (3) W is known to cause a solution strengthening effect due to the difference in atomic radii between itself and iron.⁸⁾ In addition, the low diffusion constant is considered to delay the migration of grain boundary, and then raise the recrystallization temperatures.¹⁰⁾ Previous studies have

shown that various kinds of carbide phases such as $M_{23}C_6$, M_6C , M_7C_3 , M_2C , and M_3C can precipitate simultaneously in the present steels and their morphology and volume fraction was complex depending on heat treatments and operating temperatures.⁴⁾ The trace elements such as Mn and B are expected to change the carbon activity or interface energy, thereby change the nucleation site, the carbide phase stability, and its morphology.

The main purpose of this study is to clarify the effect of Mn and B content on creep properties in 0.06C–2.25Cr–1.6W–0.1Mo–0.25V–0.05Nb steels with a particular emphasis on the microstructural stability. The microstructural evolution was evaluated from the point of carbide precipitation kinetics and alloying partitioning.

2. Experimental Procedure

Materials with three different levels of Mn-content and two levels of B-content were vacuum induction melted and processed by hot forging into 15 mm-thick plates. The chemical compositions of materials are given in Table 1. The plates were normalized for 30 min at 1323 K followed by air-cooling, and then tempered for 1 hr at 1043 K followed by air-cooling. Some of these plates were aged for from 1 000 to 10 000 hr at 873 K and 923 K.

The creep rupture tests were carried out by using mono

Table 1. The chemical compositions of the steels studied (in mass%, Bal. Fe).

	C	Si	Mn	Cr	Mo	W	V	Nb	B
40ppmB	0.01Mn	0.082	0.21	0.01	2.27	0.11	1.83	0.25	0.0039
	0.25Mn	0.081	0.21	0.24	2.28	0.11	1.85	0.25	0.0033
	0.50Mn	0.060	0.21	0.51	2.19	0.11	1.82	0.25	0.0042
75ppmB	0.01Mn	0.081	0.21	0.01	2.24	0.11	1.83	0.25	0.0074
	0.25Mn	0.080	0.21	0.24	2.23	0.11	1.83	0.25	0.0068
	0.50Mn	0.081	0.21	0.51	2.24	0.11	1.81	0.25	0.0074

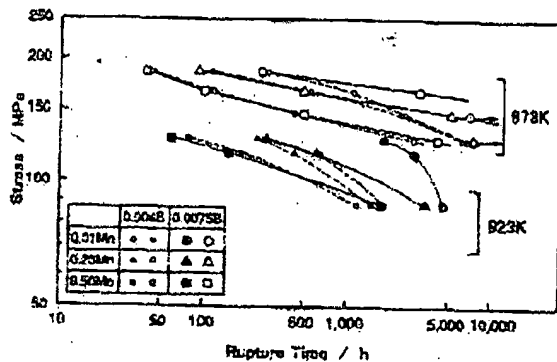


Fig. 1. Effect of Mn and B-content on creep rupture strength.

axial tensile specimens with 6 mm in diameter and 30 mm in gauge length at 873 K and 923 K. In some specimens, the creep strain was monitored during the creep test. The microstructure of the specimen crept or aged for a long time was examined at both light and electron optical levels. Transmission electron microscope observations were carried out by using thin foils from the specimens crept 2% in strain and aged for a long time at 923 K. The precipitates were also identified using extraction replica by transmission electron microscope (HITACHI-U700H) operated at 100 kV with EDX (Kevex delta-3). The amount of precipitates was estimated by the quantitative chemical analysis and X-ray diffraction intensity of the extracted residues from the aged specimens.

In order to examine the effect of alloying elements on phase stability and the alloying partitioning, the corresponding equilibrium phase diagrams were calculated using thermodynamic software, THERMOCALC.⁽¹⁾

3. Experimental Results

3.1. Creep Rupture Properties

Optical microscope observation has shown that all the present specimens normalized and tempered consist of a fully tempered bainitic phase without α -ferrite. It was confirmed that the tensile properties are little affected by Mn- and B- content.

The effect of Mn- and B-content on creep rupture time of 0.06C-2.25Cr-1.6W-0.1Mo-0.25V-0.05Nb-Mn-B steels normalized and tempered is shown in Fig. 1. It can be seen that the creep rupture strength has increased with decreasing Mn-content at 873 K and 923 K. Another important point is that the increase in B-content slightly reduces over a shorter time, but exhibits a remarkable increase for a longer exposure time over 500 hr. The effect of B is optimized in the specimens with a lower amount of Mn at 873 K, though it reduces at a lower

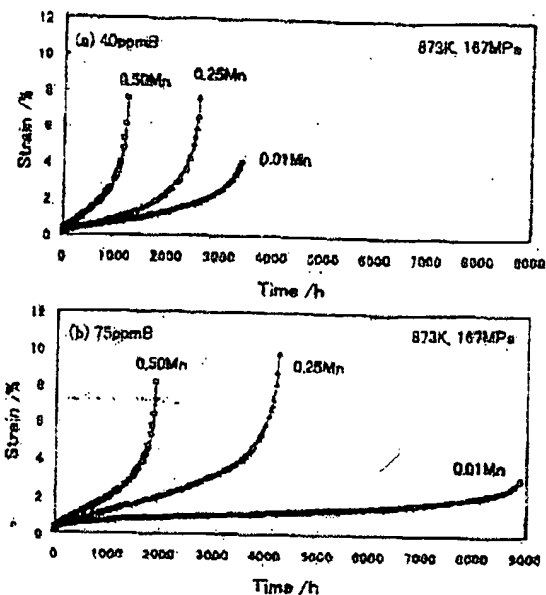


Fig. 2. Creep-strain curves under 167 MPa in stress at 873 K.

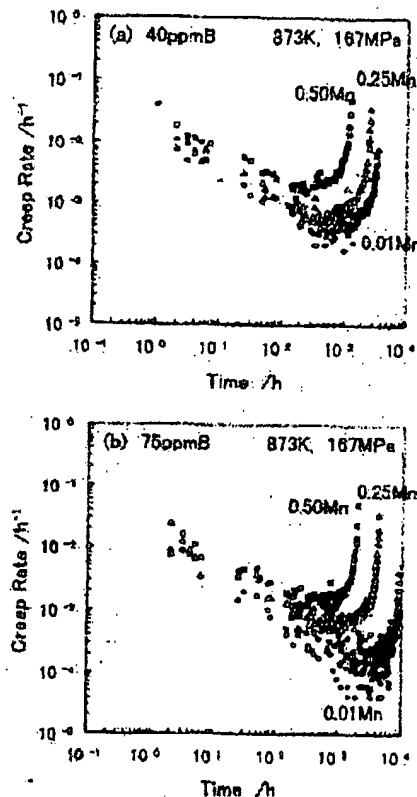


Fig. 3. Creep-rate curves under 167 MPa in stress at 873 K.

stress at 923 K.

The creep curves and creep-rate curves tested at 873 K at an applied stress of 167 MPa are shown in Figs. 2 and 3 respectively. The creep curves consist of a primary or transitional creep region, where the creep rate decreases with time, and a tertiary or accelerational creep region, where the creep rate increases with time after reaching

a minimum creep rate. It can be observed that the reduction in Mn-content has reduced the creep rate in every creep period. On the other hand, the increase in B-content changes the creep rate slightly during the primary creep stage, but delays the transition from the primary to the tertiary creep region. It is thus considered that the creep strengthening mechanisms are different between the reduction in Mn and the increase in B-content. Figure 4 summarizes the effect of Mn- and

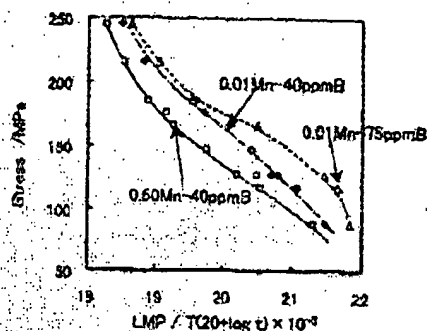


Fig. 4. The creep strength as a function of Larson-Miller parameter.

B-content on the creep rupture strength as a function of Larson-Miller Parameter (LMP), in which 20 is chosen as the LMP constant. It is confirmed that the reduction in Mn-content contributes to the creep resistance between 18.5 and 21.5 in a LMP. On the other hand, the increase in B-content contributes to that over 19.5 in LMP.

Figure 5 shows the microstructure of cross sections from specimens ruptured at 923 K at the applied stress of 88.2 MPa. It can be seen that an increase in Mn-content enhances the recrystallization and cavity growth. In the specimens with 40 ppmB steels, the creep cavities have mainly initiated and propagated along ferrite/ferrite grain boundaries, which have been newly formed by a dynamic recrystallization. An increase in B-content, however, remarkably retarded the dynamic recrystallization and thereby suppressed the localization of creep strain. In specimens with 75 ppmB, the initiation site of creep cavities seems to be former austenite grain boundaries, but the cavities propagate into ferrite grains that are locally formed around former grain boundaries as shown in Fig. 6(a). As shown in Fig. 6(b), however, a long exposure time at a low applied stress has promoted the dynamic recrystallization and then ruptured at ferrite/ferrite boundaries even in the specimens with a higher

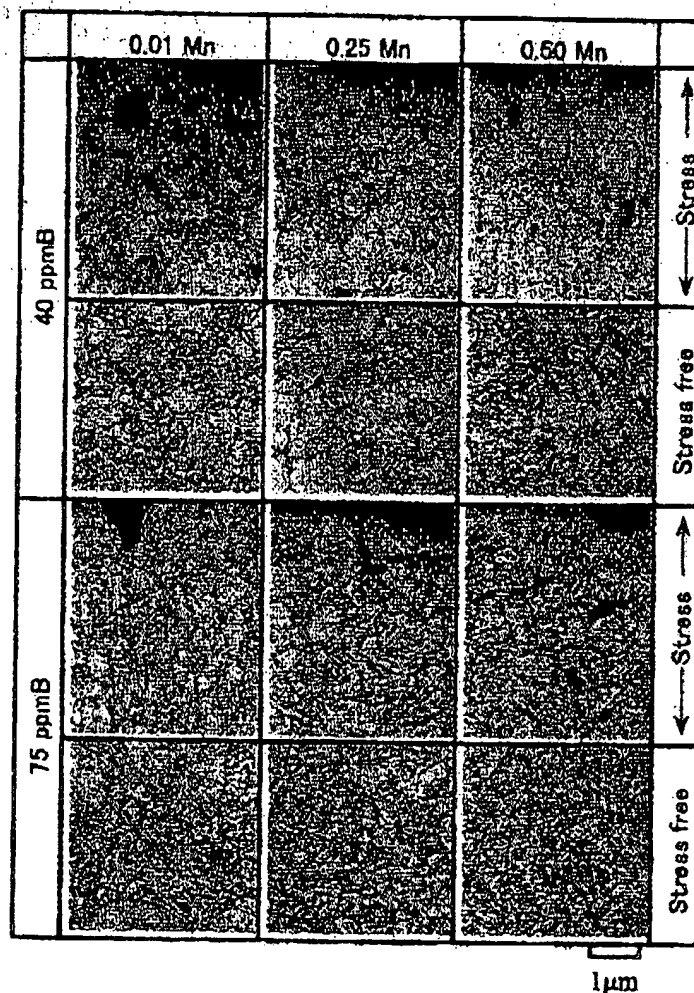


Fig. 5. Microstructures of ruptured cross section under 88.2 MPa at 923 K.

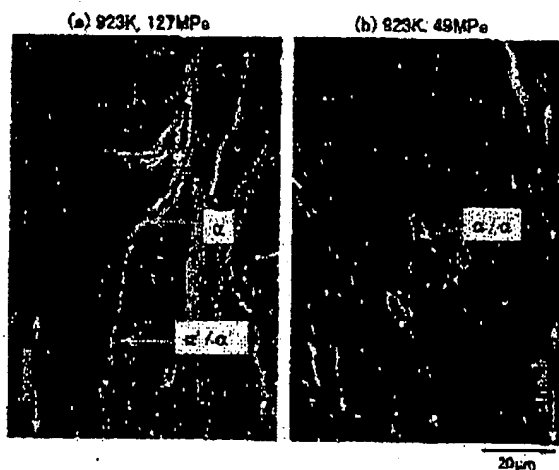


Fig. 6. SEM images of the initiation of creep cavities in the specimens with 0.01Mn-75ppmB.

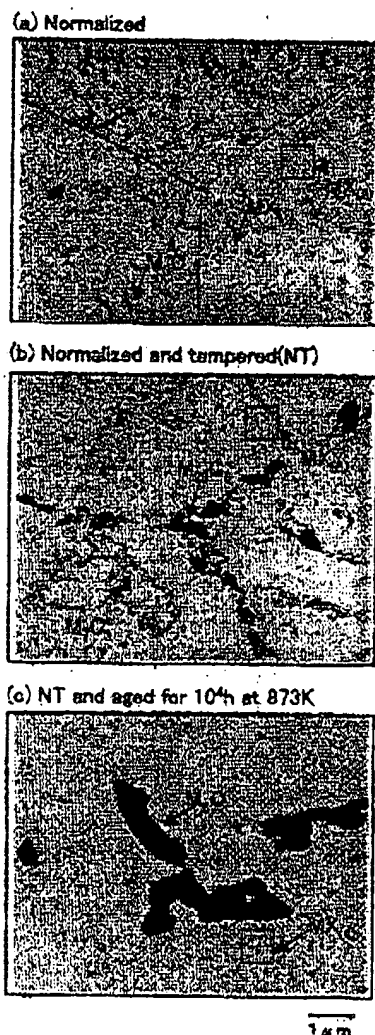


Fig. 7. TEM images of extraction replicas from 0.50Mn-40ppmB steels normalized, normalized and tempered, and aged for 10 000 hr at 873 K.

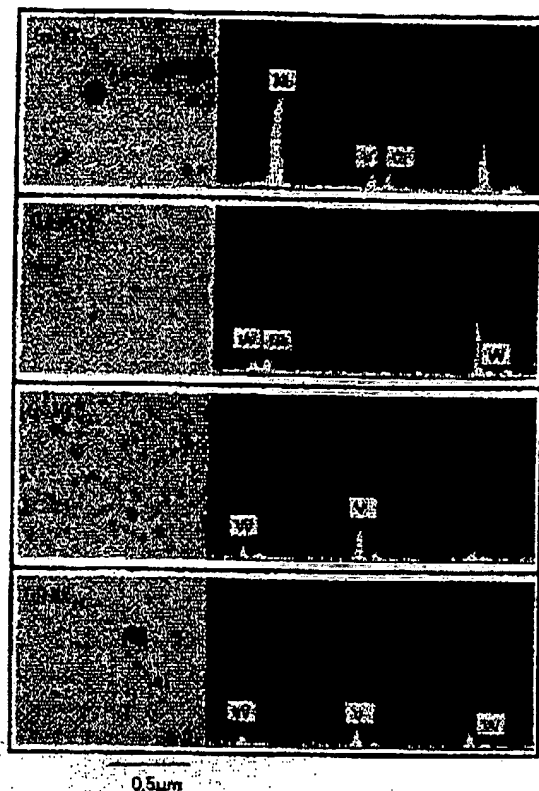


Fig. 8. TEM images of MX from extraction replica from 0.50Mn-40ppmB steels normalized, normalized and tempered, and aged for 10 000 hr at 873 K.

amount of B.

3.2. Microstructure Evolution during Long Time Aging

Figures 7 and 8 show transmission electron micrographs of extraction replica from the specimens normalized, normalized and tempered, and aged for 10 000 hr at 873 K. In the specimens normalized, Fe_3C type carbide has been observed inside grains. In addition, the fine precipitates have been identified as NbN and NbC , which can be distinguished from the compositions since the former mainly consists of Nb and the latter includes the small amount of W as shown in Fig. 8. In the case of the specimen tempered, M_{23}C_6 type carbide which contains a higher amount of Fe is observed to precipitate along former austenite grain boundaries. Inside grains, fine MX type carbides consisting of V and W has precipitated with high density along lath interfaces and dislocations. M_7C_3 type carbide is also observed inside grains in the tempered specimens. In the specimens aged for a long time at 873 K and 923 K, coarse M_6C type carbide, which contains more than 60 mass% of W, has extensively observed along grain boundaries and inside grains. Table 2 shows the compositions for each precipitate obtained by a quantitative analysis using EDX. It seems that the tempering promotes the precipitation of M_{23}C_6 , and evolves Fe_3C into M_7C_3 with a concentration of Cr. The following aging makes M_{23}C_6 and M_7C_3 evolve into M_6C with a concentration of W. TEM observation has suggested that the dynamic

Table 2. The chemical composition determined, (mass%)

	Cr	Mn	W	Fe
M ₂₃ C ₆	2.3	2.3	4.6	80.8
M ₇ C ₃	62.0	0.8	3.4	44.0
M ₆ C	25.3	1.0	12.2	61.2
M ₆ C	6.6	2.5	60.5	30.3

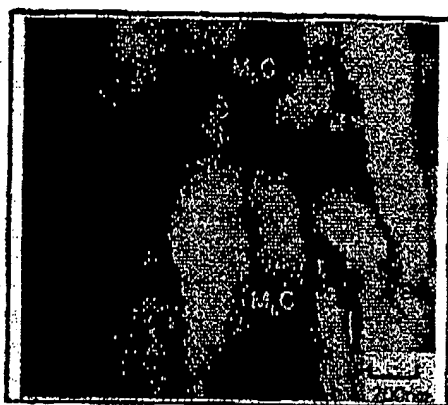


Fig. 9. TEM image from a thin foil in the 0.50Mn-40ppmB steel crept 2% in strain at 923 K.

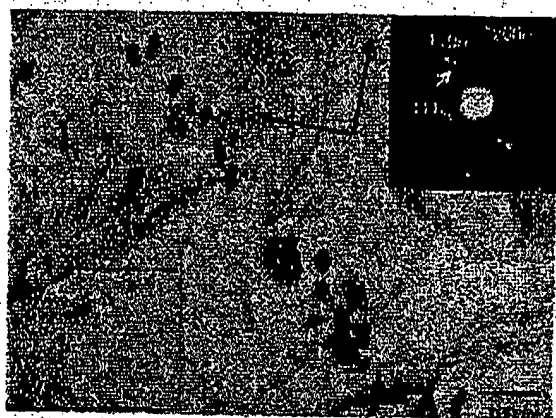


Fig. 10. TEM image from a thin foil in the 0.50Mn-40ppmB steel aged for 10000 hr at 823 K.

recrystallization has been enhanced around the coarse M₆C when the specimens are crept as shown in Fig. 9. In contrast to the above coarse carbides, the fine MX have little changed in size and composition during long-term aging. Figure 10 shows a TEM image of the specimen aged taken with a high magnification. Two types of MX, in which spherical particles with more than 20 nm in diameter have been identified as (V, W)C and the platelet particles with less than 10 nm in diameter have been identified as Nb(C, N), have often observed to pin the dislocations.

Figure 11 shows the amount of the constituent elements in the residues extracted from the specimens normalized, tempered, and aged for 3000–10000 hr at 873 K and 923 K. In the normalized specimens, Nb, W, and Fe are detected. In the case of specimens tempered at 1043 K, the main constituent elements of precipitates are Fe, Cr, V, W, and Nb. Following aging at 873 K and 923 K enhances the precipitation of W, but dissolves a small

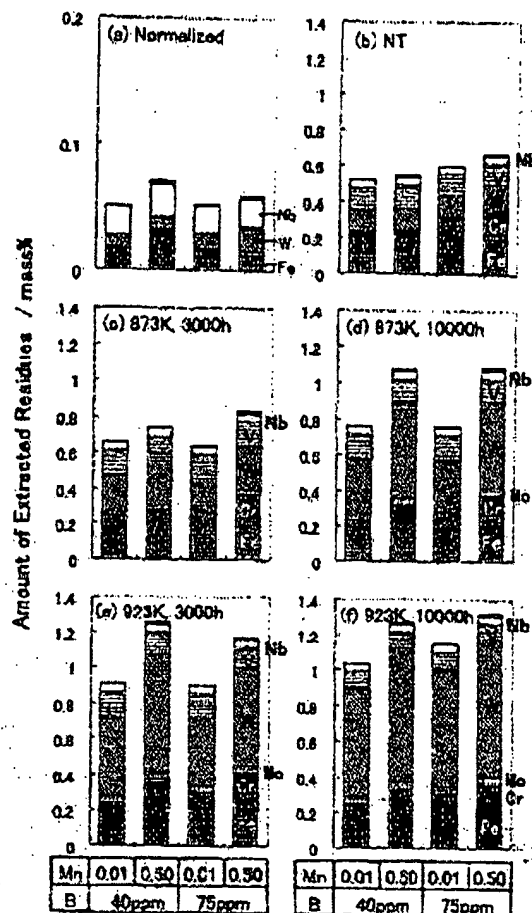


Fig. 11. Change in the amount of extracted residues in specimens normalized, normalized and tempered, and aged.

amount of Cr and V. It is noted that the increase in Mn-content drastically promotes the partitioning of Fe and W to precipitates during tempering and aging. The influence of B-content on the amount of precipitates seems to be smaller than that of Mn-content except that Fe partitioning into precipitates slightly increases. The amounts of V and Nb precipitated have been almost similar in every specimen.

Figure 12 shows the intensity ratio of X-ray diffraction spectra for M₂₃C₆, M₇C₃, and M₆C taken from the extracted residues from the specimens normalized and tempered, and aged up to 10000 hr at 873 K and 923 K. The volume fraction of each carbide is estimated by using the X-ray diffraction ratio to that of VC [(V_{C(120)} + V_{C(120)} + V_{C(111)})/3] as follows; i.e.,

$$\{[M_{23}C_{6(420)} + M_{23}C_{6(422)} + M_{23}C_{6(531)}/3]/VC$$

$$[M_{7}C_{3(150)} + M_{7}C_{3(222)}]/2]/VC$$

$$[M_{6}C_{(400)} + M_{6}C_{(331)} + M_{6}C_{(422)}]/3]/VC,$$

respectively. In the above expression, the subscripts refer to the indexes of X-ray diffraction for each crystal lattice structure. In the normalized and tempered conditions, the intensity of M₂₃C₆ has increased with the increasing

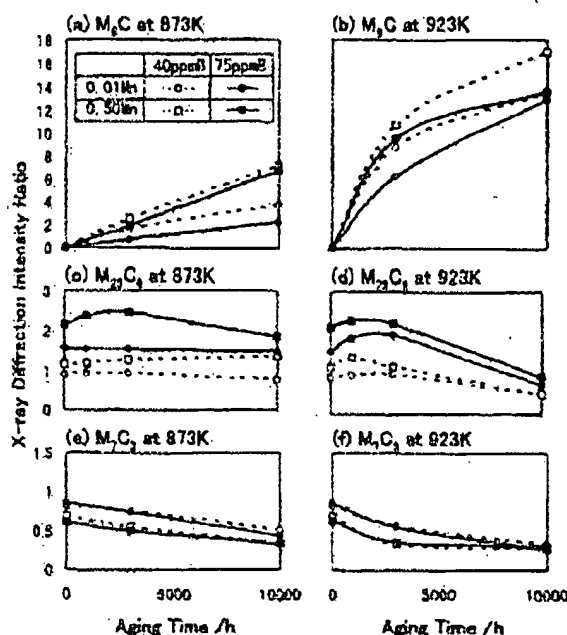


Fig. 12. The effect of Mo and B-content on the volume fraction of precipitates.

B-content and M_6C has slightly reduced with increasing Mn content. An important reaction by long-term aging is that the volume fractions of $M_{23}C_6$ and M_7C_3 are reduced but that of M_6C is drastically increased instead. The growth rate of M_6C is, however, reduced by a reduction in Mn-content. In addition, in the specimens with a higher amount of B, the volume fraction of $M_{23}C_6$ is kept higher during long-term aging. These results suggest that Mn leads to a stabilization of M_6C and B is a potent element to stabilize $M_{23}C_6$.

Figures 13 and 14 show the effect of B-content on the morphology and dispersion of precipitates. It is confirmed that an increase in B-content leaves the fine $M_{23}C_6$ on the former austenitic grain boundaries even after aging for 10 000 hr at 873 K. As for the precipitation morphology inside grains, it can be seen that MX is localized with high density around lath interface, and additionally, filmy precipitates cover the lath interface in the specimens with higher amount of B.

4. Discussion

The present study has shown that the creep properties of 0.06C-2.25Cr-1.6W-0.1Mo-0.25V-0.05Nb steels have changed to a great extent by Mn or B-content. In addition, it is found that Mn and B-content affects the morphology of carbides, dynamic recrystallization behavior, and creep cavity formations.

One of the most significant results is that a reduction in Mn-content lowers the minimum creep rate, resulting in the increase of the creep rupture strength. From the point of precipitation properties, it is found that the creep rate at the primary creep stage has a good relationship with the growth rate of M_6C . It appears that, therefore, the growth of M_6C is retarded with reducing Mn-content. This also means that the content of W in solution is kept

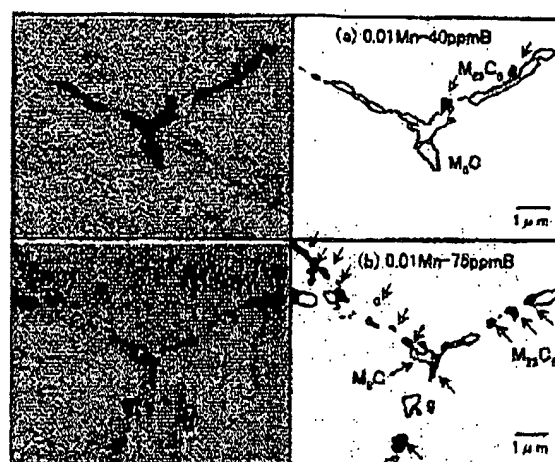


Fig. 13. TEM images showing the precipitates along grain boundaries in the specimens aged for 10 000 hr at 873 K.

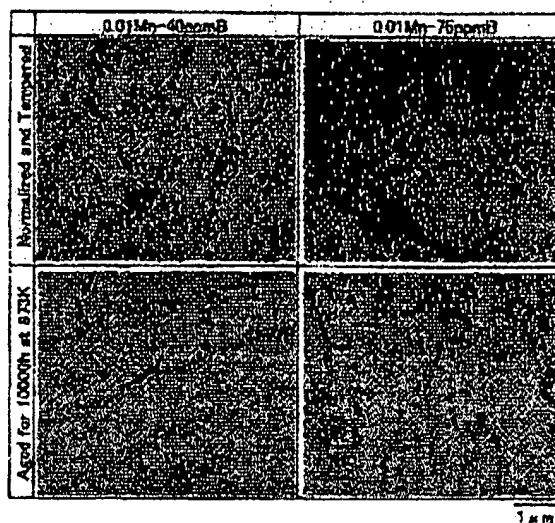


Fig. 14. TEM images showing the effect of B-content on a morphology of precipitates inside grains.

higher in the specimens with lower amount of Mn, since W is a main constituent element of M_6C . Several features on the effect of dissolved W on the creep strength are noticeable. It is widely recognized that W has a strong solution strengthening effect due to the difference in atomic radii between itself and iron.⁹⁾ It is also notable that its slow diffusion retards the migration of interface, and then raises the recovery and recrystallization temperatures.⁹⁻¹⁰⁾ In addition, Monma *et al.* have shown that the interaction between dislocations and dissolved W is strong due to the Interstitial-Solute atmosphere and explained the mechanism of a solution strengthening due to W in low alloy steels.¹²⁻¹⁴⁾ In the present creep test conditions, the creep rate in the primary creep stage has been significantly reduced, and this stage has been prolonged with increasing the dissolved W. This suggests that the dislocation mobility reduces due to the increase in dissolved W, resulting in a delay of the dynamic re-

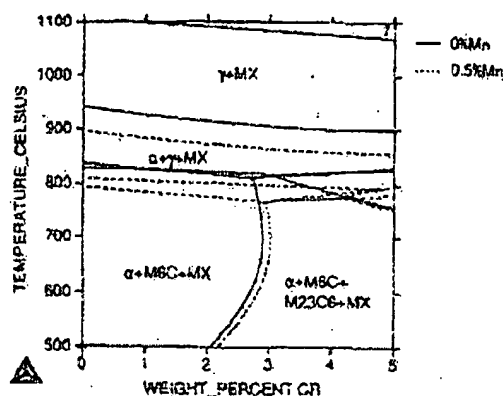


Fig. 15. Calculated phase diagram of 0.06C-2.25Cr-1.6W-0.1Mo-0.25V-0.05Nb-(0.5Mn) by using Thermo-Calc.

crystallization.

Calculated phase diagrams of 0.06-2.25Cr-1.6W-0.1Mo-0.05Nb with 0% Mn and 0.5% Mn by using Thermo-Calc are shown in Fig. 15. According to the equilibrium phase diagrams, precipitates expected for the specimens aged at temperatures between 873 K and 973 K are MX, $M_{23}C_6$, and M_6C . A big difference caused by the reduction in Mn-content is a rise in $(\alpha + M_{23}C_6 + M_6C)/\gamma$ transformation temperature and an enlargement of $M_{23}C_6$ equilibrium region. In addition, the thermodynamic calculation has also shown that the Gibbs free energy of α -phase relatively reduces by 5% and increases that of M_6C by 5% with reducing Mn-content from 0.5 to 0%. This suggests that the reduction in Mn-content leads to the stabilization of bainite matrix phase, but reduces the stabilization of M_6C . It may be understood that the mass transport and microstructure evolution is retarded by the reduction in Mn-content.

Another significant result is that an increase in B-content changes the creep rate slightly in the primary creep stage, but remarkably prolonged the primary creep stage, and then delayed the tertiary creep stage. Microstructures observations have shown that a dynamic recrystallization during creep is inhibited in the specimens with a higher amount of B. It is found that there is little difference in total amount of M_6C between the specimens with lower B and higher B. In the specimens with a higher amount of B, however, finer $M_{23}C_6$, which precipitated during tempering, has been left along grain boundaries after long-term aging. This suggests that an increase in B-content stabilizes $M_{23}C_6$ which tends to precipitate along grain boundaries. SEM and TEM observation has characterized the effect of B-content on microstructural degradations as follows. Generally, slide of former austenite grain boundaries enhances the stress concentration at the meeting grain boundaries, leading to the dynamic recrystallization at high temperatures. In the specimens with a higher amount of B, however, the fine $M_{23}C_6$ is found to cover the former austenite grain boundaries with high density. Therefore, it is considered that the $M_{23}C_6$ places an obstacle for the grain boundary sliding and then inhibits the stress concentration and the following dynamic recrystallization.

Several works have already recognized that B is easy to segregate to former austenite grain boundaries and increase the cohesive strength of grain boundaries, resulting in the good hardenability by suppressing the nucleation of ferrite.¹⁵⁻¹⁷⁾ On the other hand, B often makes precipitates such as BN, $M_{23}(C, B)_6$, $M_3(C, B)$, Fe_2B , and Boron constituent in low alloy steels.¹⁵⁾ In the present specimens, the precipitate along grain boundaries is identified as same crystal structure as $M_{23}C_6$ by the analysis of electron diffraction patterns. It is now impossible to distinguish between $M_{23}(C, B)_6$ and $M_{23}C_6$ by electron and X-ray diffraction analysis. However, considering that an increase in B-content enhances the $M_{23}C_6$ -type carbide and keeps it during a long time aging, B-partitioning is expected to stabilize the $M_{23}C_6$ -type carbide.

There is another feature on the precipitate morphology in the specimens with higher amount of B. As shown in Fig. 14, MX has localized with a high density around the lath interface, in addition, filmy precipitates covered the lath interface after tempering and following aging. It is explained that the increase in B-content form the high energy lath boundary after normalizing, and as a result, localize the MX and filmy precipitates along the lath boundaries. These filmy precipitates have not been identified yet. Some works, however, have exhibited the possibility of $M_{23}(C, B)_6$ precipitation along lath interfaces not only along former austenite grain boundaries.¹⁹⁾ It is considered that the dense precipitation and/or filmy precipitation covering the lath interfaces inhibit the boundary migration and then suppress the dynamic recrystallization.

From these considerations, the following pictures can be obtained to explain the creep deformation properties in 0.06C-2.25Cr-1.6W-0.1Mo-0.25V-0.05Nb steels. The creep strain is controlled by the amount of W in solution, which retards the dislocation recovery and increases a work hardening rate. On the other hand, the stabilization of $M_{23}C_6$ and/or $M_{23}(C, B)_6$ suppresses the grain boundary sliding and migration, and as a result, delays the tertiary creep stage. As a result, it is concluded that the reduction in Mn is effective between 18.5 to 20.5 in LMP, on the other hand, the increase in B is effective over 19.5 in LMP due to the above different strengthening mechanisms.

5. Conclusions

The effects of Mn and B-content on creep properties of 0.06C-2.25Cr-1.6W-0.1Mo-0.25V-0.05Nb have been investigated from the point of microstructural stability. With decreasing Mn-content from 0.5 mass% to 0.01 mass%, the creep rate has been reduced, and as a result, the lifetime to rupture has been increased. The increase in B from 40 ppm up to 75 ppm has also increased the lifetime due to delaying the tertiary creep stage.

The important precipitates controlling the creep deformation are MX, $M_{23}C_6$, and M_6C . The MX is effective to pin the dislocations and then increase the creep resistance. $M_{23}C_6$ mainly precipitates along former

grain boundaries when the specimens are tempered just behind A_{c1} temperatures. The M₂₃C₆, however, evolve to M₆C with a concentration of W.

The reduction in Mn-content delays the evolution into M₆C, resulting in the increase in the amount of W in solution. It is found, therefore, that the minimum creep rate is controlled by the amount of dissolved W. On the other hand, an increase in B-content stabilizes M₂₃(C, B)₆ along grain boundaries, which suppress the grain boundary sliding and migrations, and thereby the dynamic recrystallization.

It is concluded that the amount of solute W governs the creep resistance mainly in the primary creep stage, and precipitates along grain or lath boundaries affect the transition to the tertiary creep in 0.06C–2.25Cr–1.6W–0.1Mo–0.25V–0.05Nb.

Acknowledgments

The authors would like to thank Dr. S. Kobayashi, the General Manager of Corporate Research and Development, Sumitomo Metal Industries, Ltd., for permission to publish this paper. The authors would like to thank T. Ohsawa, Sumitomo Metal Technology, Ltd., for his continuous encouragement and assistance in experiments.

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